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IONIZATION OF LIQUID CARBON DISULPHIDE BY X-RAYS

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ABSTRACT

The ionization was measured in a layer of liquid between flat aluminum disks with spacings of 1 and 0.3 mm. Fields up to 60 kv per cm were used and the current voltage curve rose continuously but at a decreasing rate in this range. A plot of the reciprocal of the current against the reciprocal of the field is a straight line above 20 kv and can be extrapolated to infinite field. The form of curve is consistent with the theory of columnar recombination and the intercept at infinite field gives the rate of production of ions. Comparison with the radiation in roentgens gives the ionization per unit volume in liquid carbon disulphide as 2,600 times that of air under standard conditions. The absorption is 1,910 times that of air and the energy of ionization per ion pair about 0.75 times that of air. The shape of the curve and the columnar theory give the diameter of the columns as 5.8×10^{-6} cm and the density of ionization in the columns as 2.3×10^{16} ions per cm^3.

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I. INTRODUCTION

The ionization of dielectric liquids by X-rays was discovered by J. J. Thomson [1] in 1895 and the related case of ionization by gamma rays was studied in detail by Jaffé [2] and his associates in the period 1906 to 1913. The properties of ionized liquids are comparable to those of very dense gases. The mobility of the ions and their rate of recombination are very small (in liquid carbon disulphide both are about 10^{-4} of the values for air at one atmosphere).[3] The current voltage curves rise rapidly toward saturation with fields up to 1,000 volts per cm but with further increase in field the current continues to increase and in the range 1,000 to 5,000 volts the increase is nearly linear. Some of Jaffé's experiments seemed to indicate that this linear increase was absent in very pure liquids but his later papers reject this result. In a comprehensive theoretical paper [4] he was able to show that Langevin's theory of columnar recombination could

[1] J. J. Thomson, Nat., 53,378(1895).
[2] Jaffé, Ann. der Phys., 25,257(1908);28,326(1909).
[3] Van der Bijl, Ann. der Phys., 39,170(1912).
[4] Jaffé, Ann. der Phys., 42,303(1913).

account for the lack of saturation in liquids and gases ionized by alpha and gamma rays. The absorption of a quantum of X-rays or gamma rays gives rise to a single high-speed electron. This traverses the gas or liquid leaving a dense trail of ions and these may be so close together that the highest fields will not separate them before some of them recombine. Insofar as the ions from separate columns do not recombine with each other, the current will be proportional to the number of quanta absorbed but will be less than the total production of ion pairs. Jaffé estimated that in liquids ionized by gamma rays only a tenth of the ions are removed from the column while from alpha ray tracks only one in a thousand escapes. These estimates are based on the assumption that the average energy expended per ion pair is the same as in air. Published results obtained with fields of less than 5,000 v/cm give no basis for an experimental value of the actual number of ions produced in a liquid. It has been our purpose to extend current voltage curves to much higher fields in an attempt to measure the actual production of ions by X-rays in liquids. Jaffé's results and our preliminary experiments indicated that carbon disulphide was a promising liquid for the experiment.

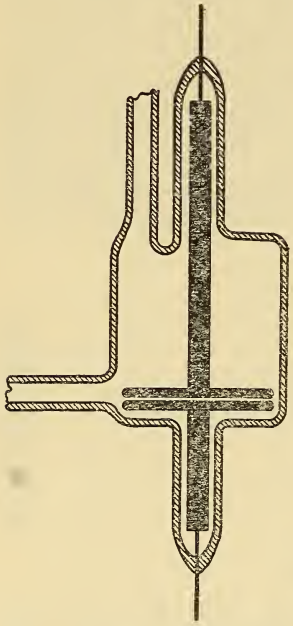

FIGURE 1.—*Ionization chamber.*

II. IONIZATION CHAMBERS

The attainment of high fields requires smooth rounded surfaces close together and we have used a simple two-electrode chamber sealed in a pyrex glass bulb as illustrated in figure 1. The electrodes are aluminum disks 4.5 cm in diameter with the edges rounded. Plate separations of 1 and 0.3 mm were used. This bulb construction is adapted to obtaining pure dry liquid in the chamber, but it was not possible to evaluate accurately the radiation flux through the end of the bulb.

For quantitative comparison of liquid and air ionization the following chamber was made. Two plates of aluminum were separated by mica rings of 8 cm outside diameter and 4 cm inside diameter. These rested in a crystallizing dish. A mica cover limited evaporation and a lead ring restricted the vertical X-ray beam to the 4-cm hole in the mica spacers. Here the radiation flux could be closely estimated and the ionized volume of liquid is not subject to edge corrections.

III. PURIFICATION OF LIQUID

Commercial carbon disulphide has a high conductivity and must be purified. The conducting impurities are probably water and hydrogen sulphide. The procedure was to pour the liquid into a bulb containing quicklime and hold it at liquid air temperature in high vacuum while baking out the ionization chamber. Then the liquid was slowly distilled in vacuum through phosphorus pentoxide into a

trap, and finally into the ionization chamber. The resulting liquid had a specific resistance of more than 10^{14} ohms. This gives a leak of less than 1 percent of the ionization current but very much higher resistance can be obtained with elaborate precautions.[5] In using the open chamber, this was first dried by warming and the purified liquid poured in. The leak here was about 10 times that in the vacuum chamber though the experiments were made in cold dry winter weather.

IV. RADIATION

Slightly filtered X-rays from a tungsten target tube operated at 120 kv constant potential and a current of 5 ma or less, passed through the chamber normal to the electrodes at a distance of about 50 cm from the target. The ionization in the liquid was compared with air ionization by replacing the chamber by a roentgenometer calibrated to read in roentgens for the quality of radiation used. The quality of radiation expressed in terms of the true effective wave length in aluminum was 0.44 A outside the chamber and 0.27 in the liquid.[6]

The ionization in a small chamber depends on the wall material as well as the ionized medium. For carbon disulphide and aluminum the effect is small for both have comparable X-ray absorption so that the loss of electrons by the liquid nearly compensates for the gain from the metal. Taking the difference in ionization with different electrode spacings should eliminate the wall effect, but because of the increased experimental error this procedure was not used.

V. ELECTRICAL MEASUREMENTS

The voltage source for the ionization chamber was a very steady constant potential X-ray generator. The leads to the chamber were covered and shielded to avoid corona and air ionization. Currents were of a magnitude to measure with a sensitive galvanometer. The response upon admitting or cutting off the radiation was nearly instantaneous, but the dark current dropped at a decreasing rate for minutes every time the voltage was increased. This comes in part from electrical clean-up of the liquid and in part from polarization. With fields up to 20 or 30 kv per cm the dark current is small. At higher fields it rapidly becomes large and unsteady, and above 60 kv the measurements are too inaccurate to be useful. The maximum field strength was about the same for plate separations of 1 or 0.3 mm for dry liquid in vacuum and for the liquid exposed to air.

VI. THE CURRENT VOLTAGE CURVE

All results reduced to the same current scale are included in figure 2. Open circles give measurements with a 1 mm spacing and crosses apply to the 0.3 mm spacing with a current correspondingly smaller. Tests with different intensities of radiation showed that above 2 kv per cm the current is proportional to the intensity. Hence we conclude

[5] Van der Bijl, Ann. der Phys., **39**,170(1912).

[6] The roentgen is the quantity of radiation which will give in 0.001293 g of air 1 esu of ion pairs. The true effective wave length is the wave length of homogeneous radiation which will be reduced in the same ratio by an infinitesimal layer of aluminum. In media comparable with aluminum in atomic number (and only in these) the radiation can be treated as a homogeneous radiation of this wave length. L. S. Taylor, BS J.Research **5**,517(1930);RP212.

that above this point the form of the curve is not influenced by intercolumnar recombination. There was no observable difference between the curves obtained in the pure liquid and in the liquid exposed to air. This result does not support the view that traces of impurity modify the form of the curve.[7]

Jaffé[8] has derived a general expression for the fraction of ions I_X/I_∞ drawn from a column by a field X when the ion pairs are initially distributed in a cylinder of diameter d with a density of N pairs per cm of column length.

$$\frac{I_\infty}{I_X} = 1 + \frac{\alpha N}{7.85\, duX\ F(X)} \tag{1}$$

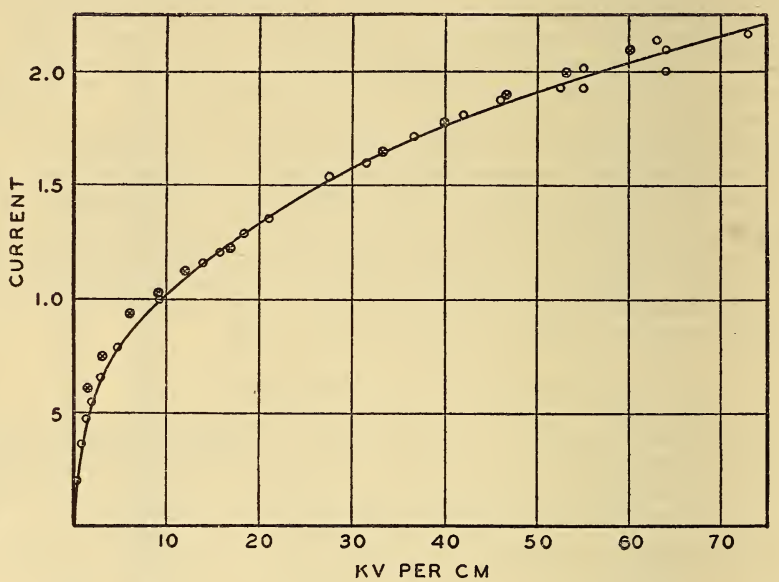

FIGURE 2.—*Current voltage curve in liquid carbon disulphide.*
Circles with 1 mm between electrodes, crosses 0.3 mm.

Here α is the recombination coefficient, 9×10^{-10}, and u the mobility of the ions, 0.66×10^{-3} cm per sec, per volt per cm. $F(X)$ is a complicated function which approaches 1 for high fields (over 10^4 volts per cm). The form of the equation indicates that a plot of $1/I_X$ versus $1/X$ will be nearly linear. Figure 3 gives the curve of figure 2 on this scale and the resulting curve conforms to the theoretical prediction. In view of the theory it is safe to make a linear extrapolation from the observed points to $1/X=0$. The intercept gives (in arbitrary units) the reciprocal of the current at infinite voltage and is a measure of the actual rate of production of ions by the X-rays. Measurements at the highest fields gave about three-quarters of the saturation current.

VII. COMPARISON WITH AIR IONIZATION

The ionization produced in the open chamber with 1 mm spacing was compared with the reading of the roentgenometer. The radiation flux corrected for absorption in the top plate of the liquid chamber

[7] Jaffé, Ann. der Phys., 28, 326(1909).
[8] Jaffé, Ann. der Phys., 42, 303(1913).

was 0.129 roentgens per sec (0.129 esu per cm^3 of free air under standard conditions). The current in the liquid extrapolated to infinite field was 1.12×10^{-7} amp per cm^3 or 336 esu per cm^3 per sec. Hence the ionization per unit volume in liquid carbon disulphide is 2,600 times that in air.

The ionization in any medium is proportional to the energy absorbed divided by the average energy required to produce an ion pair or $\mu\rho/E$ where μ is the mass absorption coefficient, ρ the density and E the energy per ion pair. Thus

$$\frac{(\mu\rho/E) \text{ for } CS_2}{(\mu\rho/E) \text{ for air}} = 2{,}600$$

The experimental value of μ for air for radiation of this quality is 0.35.[9] The value μ for CS_2 computed from the monochromatic values for C and S at 0.27 A (the effective wave length in Al for the radiation) is 0.67. The density ratio is 1,000. Taking the average energy expended per ion pair in air as 33 electron volts we find the average energy in liquid carbon disulphide is 24 volts. A published value [10] of the ionization of carbon disulphide vapor by X-rays indicates a value of 26 electron volts. We conclude that within the range of experimental uncertainty the energy required to ionize carbon disulphide is the same in the liquid phase as in the gas phase.

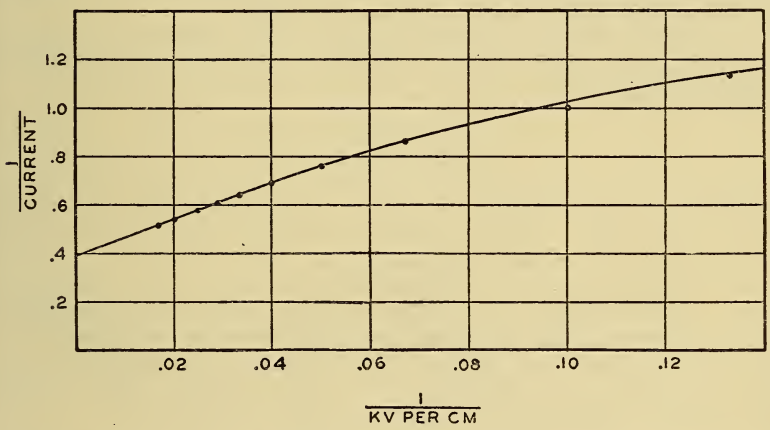

FIGURE 3.—*Curve of figure 2 plotted with reciprocal of current versus reciprocal of voltage.*

VIII. COLUMNAR IONIZATION

As noted above, the process of ionization consists in the ejection of a high-speed electron which traverses the liquid and produces a dense column of ions. On the basis of our experimental data and Jaffé's theory the process can be described in more detail. The secondary electrons will have an average energy of 46,000 electron volts (corresponding to 0.27 A). These will go a distance of 3.2×10^{-3} cm [11]

[9] L. S. Taylor, BS J. Research, 6, 219(1931); RP271.
[10] J. J. Thomson, Conduction of Electricity in Gases, 2, 238(1933).
[11] Rutherford Chadwick and Ellis, Radiation from Radioactive Substances, 422(1930).

through the liquid and produce in this distance 1,900 ion pairs giving an average density of 6×10^5 pairs per cm of path. At high voltages equation 1 becomes

$$\frac{I_\infty - I_x}{I_x} = \frac{\alpha N}{7.85\, duX}$$

where N is the ion density evaluated above, and all other quantities are known except d, the diameter of the column. The slope of the curve in figure 3 gives the value of d as 5.8×10^{-6} cm. (The distance between ion pairs ($1/N$) is 1.7×10^{-6} cm). The physical significance of d is probably as follows: The secondary electrons produce positive ions and tertiary electrons of about 10 volts energy which move away until they become attached to molecules to form heavy negative ions. The constant d is (apart from a small geometrical factor) the distance the electron goes before attaching. This distance is a characteristic of the liquid and an important but unpredictable factor in determining the yield of ions under a given field.

The values for the dimensions of a column lead to a value of $2.3+10^{16}$ ion pairs per cm^3 in a column. From the recombination equation in the form

$$\frac{1}{n} - \frac{1}{n_o} = \alpha t$$

it is found that this ionization will be reduced to a fifth of its initial value in 2×10^{-7} sec. About a fifth of the ions escape in zero field so this time is the life of the column. In our experiment X-ray quanta were absorbed and columns produced at the rate of 3.7×10^8 per cm^3 per sec. Thus about 74 columns per cm^3 existed at any instant. From the conductivity produced by X-rays at low voltage and the mobility of the ions one estimates the average concentration of ion pairs in zero field as 1.1×10^{10} per cm^3. Upon cutting off the radiation this will drop to half value by recombination in 0.2 sec.

IX. CONCLUSIONS

The above numerical values for the elementary processes are of interest only as an illustration of the deductions that can be drawn from the constants of the current voltage curve. The results support the assumption that the number of ions produced in a liquid by the absorption of a quantum is about the same as in a gas and that the current resulting from the ionization is greatly reduced by intra-columnar recombination.

The application of liquid ionization chambers to the measurement of X-rays and gamma rays is not new, but its possibilities are not generally appreciated.[12] With fields of the order of 20 kv per cm the current in carbon disulphide is perfectly steady and strictly proportional to the intensity and it is over 1,000 times the current from an equal volume of air. The comparison of radiations of different quality would require further research. The columnar recombination theory indicates that the degree of saturation for a given field will depend on the quality because of the variation in the number of ions per unit length of the column.

Washington, September 13, 1934.

[12] Stahel, Strahlentherapie, **31**, 582(1929).